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1.	Your reference	CDT 322
2.	Patent application number *(The Patent Office will fill in this part)*	03 SEP 2002 0220404.8
3.	Full name, address and postcode of the or of each applicant *(underline all surnames)*	Cambridge Display Technology Limited Greenwich House Madingley Rise Madingley Road Cambridge CB3 OTX
	Patents ADP number *(if you know it)*	06166441006
	If the applicant is a corporate body, give the country/state of its incorporation	United Kingdom
4.	Title of the invention	OPTICAL DEVICE
5.	Name of your agent *(if you have one)* "Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*	IP Department Cambridge Display Technology Limited Greenwich House Madingley Rise Madingley Road Cambridge CB3 OTX
	Patents ADP number *(if you know it)*	06166441009

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Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

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Signature A. Gilani Date 02 September 2002

12. Name and daytime telephone number of person to contact in the United Kingdom

Anwar Gilani
Tel: 01223 723519

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DUPLICATE

Optical device

Field of the Invention

This invention relates to polymeric optical devices comprising a layer of insoluble polymer and methods for the production thereof.

Background of the Invention

Electroactive polymers are now frequently used in a number of optical devices such as in polymeric light emitting diodes ("PLEDs") as disclosed in WO 90/13148, photovoltaic devices as disclosed in WO 96/16449 and photodetectors as disclosed in US 5523555.

A typical PLED comprises a substrate, on which is supported an anode, a cathode and an organic electroluminescent layer between the anode and cathode comprising at least one polymeric electroluminescent material. In operation, holes are injected into the device through the anode and electrons are injected into the device through the cathode. The holes and electrons combine in the organic electroluminescent layer to form an exciton which then undergoes radiative decay to give light. Other layers may be present in the PLED, for example a layer of organic hole injection material such as poly(ethylene dioxy thiophene) / polystyrene sulfonate (PEDT / PSS) may be provided between the anode and the organic electroluminescent layer to assist injection of holes from the anode to the organic electroluminescent layer.

In a typical PLED, the electroluminescent material is provided as a single layer as described in, for example, WO 99/48160 which comprises a blend of a hole transporting polymer, an electron transporting polymer and an emissive polymer. Alternatively, a single polymer may provide two or more of the functions of hole transport, electron transport and emission. The electroluminescent polymer or polymers are preferably soluble in common organic solvents to facilitate their deposition. One such class of soluble polymers are polyfluorenes which have good film forming properties and which may be readily formed by Suzuki or Yamamoto polymerisation which enables a high degree of control over the regioregularity of the resultant polymer.

It may, however, be preferred to cast multiple layers, i.e., laminates, of different polymers on a single substrate surface, so that one can achieve optimisation of separate functions, for example electron or hole charge transport, luminescence, photo-induced charge generation, and charge blocking or storage. Furthermore, it is believed that PEDT / PSS may have a

deleterious effect on the electroluminescent layer, for example by ingress of protons from PSS into the electroluminescent layer (i.e. the layer in which holes and electrons combine to form an exciton), resulting in quenching of luminescence. Accordingly, it may be desirable to provide a protective layer between PEDT / PSS and the electroluminescent layer. However, preparation of polymer laminates can be problematic due to solubility of initially cast or deposited layers in the solvents used for succeeding layers.

Layers of electroluminescent polymer may be formed by depositing a soluble polymeric precursor which is then chemically converted to an insoluble, electroluminescent form. For example, WO 94/03030 discloses a method wherein insoluble, electroluminescent poly(phenylene vinylene) is formed from a soluble precursor and further layers are then deposited from solution onto this insoluble layer. However, the chemical conversion process involves extreme processing conditions and reactive by-products that harm the performance of the finished device. Accordingly, electroluminescent polymers that are soluble in common organic solvents are preferable. Examples of such materials are disclosed in, for example, Adv. Mater. 2000 12(23) 1737-1750 and include polyfluorenes, polyphenylenes and poly(arylene vinylenes) with solubilising groups.

WO 98/05187 discloses a method of forming a multilayer device comprising the steps of depositing a poly(vinyl pyridine) layer onto PEDT / PSS and depositing a PPV precursor onto the poly(vinyl pyridine) layer. As above, this precursor requires harsh processing conditions in order to convert to a semiconducting material.

US 6107452 discloses a method of forming a multilayer device wherein fluorene containing oligomers comprising terminal vinyl groups are deposited from solution and cross-linked to form insoluble polymers onto which additional layers may be deposited. Similarly, Kim *et al*, Synthetic Metals 122 (2001), 363-368 discloses polymers comprising triarylamine groups and ethynyl groups which may be cross-linked following deposition of the polymer. The choice of polymers in both instances is constrained by the requirement that a plurality of vinyl or ethynyl moieties be present.

It is an object of the invention to provide a method for preparing polymeric optical devices comprising a plurality of electroactive layers without the need for harsh reagents or extreme processing conditions and without the need to provide functionalised units on the polymer for cross-linking.

It is a further object of the invention to provide an optical device wherein a semiconducting layer is protected by a buffer layer from the possibility of deleterious interactions with an adjacent layer of organic hole injection material.

Summary of the Invention

In a first aspect, the invention provides a method of forming an optical device comprising the steps of:

- providing a substrate comprising a first electrode capable of injecting or accepting charge carriers of a first type;
- forming over the first electrode a first layer that is insoluble in a solvent by depositing a first semiconducting polymer that is free of cross-linkable vinyl or ethynyl groups and that is, at the time of deposition, soluble in the solvent;
- forming a second layer in contact with the first layer and comprising a second semiconducting polymer by depositing a second semiconducting polymer from a solution in the solvent; and
- forming over the second layer a second electrode capable of injecting or accepting charge carriers of a second type.

Preferably, the method comprises the step of heating the first layer prior to formation of the second layer. More preferably, the first layer is heated at above the glass transition temperature of the first semiconducting polymer.

In a second aspect, the invention provides a method of forming an optical device comprising the steps of:

- providing a substrate comprising a first electrode capable of injecting or accepting charge carriers of a first type;
- forming a first layer over the first electrode by depositing a first semiconducting polymer comprising fluorene repeat units, the first semiconducting polymer being free of cross-linkable vinyl or ethynyl groups and being, at the time of deposition, soluble in the solvent;

- forming a second layer in contact with the first layer and comprising a second semiconducting polymer by depositing a second semiconducting polymer from a solution in the solvent; and

- forming over the second layer a second electrode capable of injecting or accepting charge carriers of a second type.

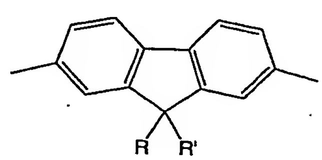
Preferably, the method comprises a step of heating the first layer prior to deposition of the second layer. More preferably, the first layer is heated at a temperature above the glass transition temperature of the first semiconducting polymer.

Preferably, the method comprises a step prior to forming the second layer of washing the first layer with a solvent in which the first semiconducting polymer is soluble. Preferably, the solvent is an aromatic hydrocarbon, more preferably an alkylated benzene and most preferably toluene or xylene.

Preferably, the first semiconducting polymer is free of cross-linkable groups other than vinyl or ethynyl groups.

Preferably, repeat units of the first and second semiconducting polymers are conjugated to adjacent repeat units to form an at least partially conjugated polymer backbone.

In a preferred embodiment of the second aspect, the fluorene repeat units preferably comprise 9-substituted or 9,9-disubstituted fluorene-2,7-diyl repeat units, most preferably optionally substituted units of formula (I):

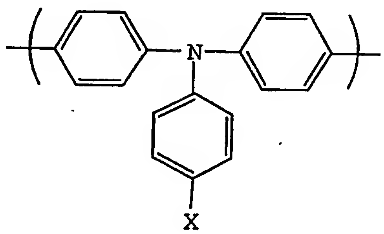


(I)

wherein R and R' are independently selected from hydrogen or optionally substituted alkyl, alkoxy, aryl, arylalkyl, heteroaryl and heteroarylalkyl, and at least one of R and R' is not hydrogen. More preferably, at least one of R and R' comprises an optionally substituted C_4-C_{20} alkyl group.

In a first preferred embodiment of the device prepared by the method of the invention, the first electrode is capable of injecting or accepting holes and the second electrode is capable of injecting or accepting electrons. In this embodiment, a layer of conductive organic material is preferably provided between the first electrode and the first layer. Preferably, the layer of conductive organic material is PEDT / PSS

In this embodiment, the first semiconducting polymer preferably comprises a hole transporting material, preferably a polymer comprising triarylamine repeat units. Particularly preferred triarylamine repeat units are selected from optionally substituted repeat units of formulae 1-6:



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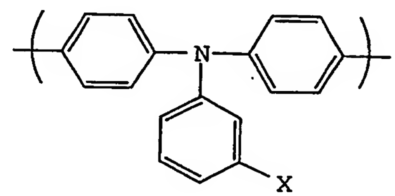

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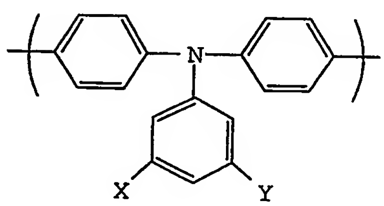

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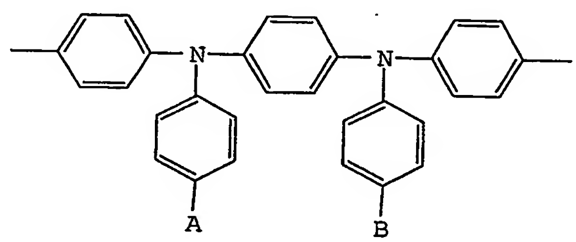

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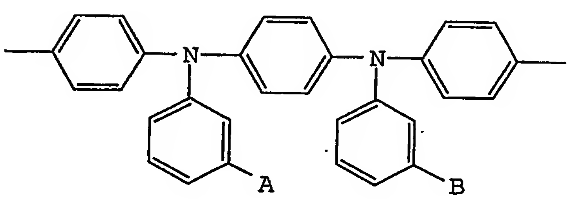

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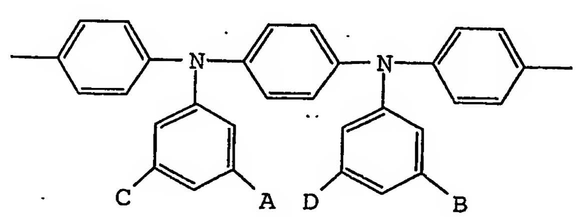
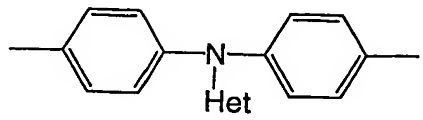


6

wherein X, Y, A, B, C and D are independently selected from H or a substituent group. More preferably, one or more of X, Y, A, B, C and D is independently selected from the group consisting of alkyl, aryl, perfluoroalkyl, thioalkyl, cyano, alkoxy, heteroaryl, alkylaryl and arylalkyl groups.

Also particularly preferred as the triarylamine repeat unit is an optionally substituted repeat unit of formula 7:



7

wherein Het is a heteroaryl. Most preferably, Het is 4-pyridyl.

Preferably, the first semiconducting polymer comprises a 1:1 regular, alternating copolymer of a fluorene repeat unit and a triarylamine repeat unit.

Preferably, a layer of conductive organic material is provided between the first electrode and the first layer. More preferably, the layer of conductive organic material is PEDT / PSS.

In a second preferred embodiment of the device prepared by the method of the invention, the first electrode is capable of injecting or accepting electrons and the second electrode is capable of injecting or accepting holes. In this embodiment, the first semiconducting polymer preferably comprises an electron transporting material, preferably the homopolymer of an optionally substituted 9,9-dialkylfluorene-2,7-diyl.

Preferably, the first layer has a thickness of less than 20 nm, more preferably less than 10 nm, most preferably in the range 3-10 nm.

Preferably, the second semiconducting polymer comprises a plurality of regions and comprising at least two of a hole transporting region, an electron transporting region and an emissive region, more preferably all three of these regions.

In a third aspect, the invention provides an optical device preparable according to the method of the invention. Preferably, the optical device is an electroluminescent device, more particularly a blue light emitting electroluminescent device. A part of the emission of the blue light emitting device may be downconverted with phosphors capable of producing red and green light by downconverting said blue light to give a white light emitting electroluminescent device.

The method of the invention enables the formation of polymer laminates wherein the first layer is particularly thin. Accordingly, in a fourth aspect, the invention provides an optical device comprising, in sequence:

- a substrate

- a first electrode capable of injecting or accepting charge carriers of a first type

- a first layer having a thickness less than 20 nm comprising a first semiconducting polymer that is insoluble in a solvent

- a second layer in contact with the first layer comprising a second semiconducting polymer that is soluble in the solvent

- a second electrode capable of injecting or accepting charge carriers of a second type.

In a fifth aspect, the invention provides a method of forming an optical device comprising the steps of:

- providing a substrate carrying a conductive organic material capable of injecting or accepting holes and capable of donating protons;

- forming over and in contact with the conductive organic material a first layer by depositing a first semiconducting polymer capable of accepting protons wherein the semiconducting polymer is, at the time of deposition, soluble in a solvent;

- forming a second layer by depositing over, and in contact with, the first layer a second semiconducting polymer from a solution in the solvent; and

- forming over the second layer a second electrode capable of injecting or accepting electrons.

Preferably, the first semiconducting polymer comprises triarylamine repeat units. More preferably, the triarylamine repeat units are selected from repeat units 1-7 described above.

Preferably, the first semiconductive polymer comprises a 1:1 regular, alternating copolymer of a fluorene repeat unit and a triarylamine repeat unit.

Preferably, a layer of inorganic material capable of injecting or accepting holes is provided between the substrate and the conductive organic material. Most preferably, the inorganic material capable of injecting or accepting holes is indium tin oxide.

Preferably, the conductive organic material is PEDT / PSS.

The first and second semiconducting polymers according to any aspect of the invention may be the same or different.

The second layer may consist solely of the second semiconductive polymer or it may be a blend comprising the second semiconducting polymer.

By "red light" is meant radiation having a wavelength in the range of 600-750 nm, preferably 600-700 nm, more preferably 610-650 nm and most preferably having an emission peak around 650-660 nm.

By "green light" is meant radiation having a wavelength in the range of 510-580 nm, preferably 510-570 nm.

By "blue organic light" is meant radiation having a wavelength in the range of 400-500 nm, more preferably 430-500 nm.

The meaning of "hole transporting", "electron transporting" and "emissive" as used herein is explained in, for example, WO 00/55927 and WO 00/46321 and as such will be apparent to the skilled person.

Brief Description of the Drawings

The present invention will now be described in further detail, by way of example only, with reference to the accompanying drawings in which:

FIGURE 1 shows a PLED or photovoltaic device prepared according to the method of the invention

FIGURE 2 shows a plot of efficiency vs. bias for a blue electroluminescent device

FIGURE 3 shows a plot of efficiency vs. bias for a red electroluminescent device

FIGURE 4 shows a plot of efficiency vs. bias for a blue electroluminescent device, with and without spin rinsing

Detailed Description of the Invention

With reference to figure 1, a PLED or photovoltaic device prepared according to the method of the invention comprises a substrate 1, an anode 2 of indium tin oxide, a layer 3 of organic hole transport material, a layer 4 of insoluble material made by deposition of a first soluble semiconducting polymer, a layer 5 made by deposition of a second semiconducting polymer and a cathode 6.

Optical devices tend to be sensitive to moisture and oxygen. Accordingly, the substrate preferably has good barrier properties for prevention of ingress of moisture and oxygen into the device. The substrate is commonly glass, however alternative substrates may be used, in particular where flexibility of the device is desirable. For example, the substrate may comprise a plastic as in US 6268695 which discloses a substrate of alternating plastic and barrier layers or a laminate of thin glass and plastic as disclosed in EP 0949850.

Although not essential, the presence of layer 3 of organic hole injection material is desirable as it assists hole injection from the anode into the layer or layers of semiconducting polymer. Examples of organic hole injection materials include PEDT / PSS as disclosed in EP 0901176 and EP 0947123, or polyaniline as disclosed in US 5723873 and US 5798170.

Cathode 6 is selected in order that electrons are efficiently injected into the device and as such may comprise a single conductive material such as a layer of aluminium. Alternatively, it may comprise a plurality of metals, for example a bilayer of calcium and aluminium as disclosed in WO 98/10621, or a thin layer of dielectric material such as lithium fluoride to assist electron injection as disclosed in, for example, WO 00/48258.

The device is preferably encapsulated with an encapsulant (not shown) to prevent ingress of moisture and oxygen. Suitable encapsulants include a sheet of glass, films having suitable barrier properties such as alternating stacks of polymer and dielectric as disclosed in, for example, WO 01/81649 or an airtight container as disclosed in, for example, WO 01/19142.

In a practical device, at least one of the electrodes is semi-transparent in order that light may be absorbed (in the case of a photoresponsive device) or emitted (in the case of a PLED). Where the anode is transparent, it typically comprises indium tin oxide. Examples of transparent cathodes are disclosed in, for example, GB 2348316.

Insoluble layer 4 preferably comprises a polymer comprising fluorene repeat units. Where the insoluble layer is located between the anode and layer 5, as per the embodiment of figure 1, it is preferably formed from a semiconducting polymer capable of transporting holes – for example a copolymer of a fluorene repeat unit and a triarylamine repeat unit as disclosed in WO 99/54385. Alternatively, the insoluble layer may be deposited over a cathode. In this instance, the insoluble layer is preferably formed from a semiconducting polymer capable of transporting electrons – for example a homopolymer of fluorene as disclosed in, for example, EP 0842208.

Insoluble layer 4 is formed upon deposition of the first semiconducting polymer. The layer as deposited may be entirely insoluble or partially insoluble. Where the first layer is only partially

insoluble, the insoluble fraction within the layer may be increased by heating of the layer as deposited. Any soluble first semiconducting polymer may be removed from the layer by rinsing in an appropriate solvent in order to leave an entirely insoluble layer.

The second semiconducting polymer according to the invention used to form layer 5 may be any semiconductive polymer that is soluble in the same solvent as the first semiconducting polymer used to form insoluble layer 4. Examples of suitable second semiconductive polymers include soluble poly(p-phenylene vinylenes), polyphenylenes and polyfluorenes as disclosed in Adv. Mater. 2000 12(23) 1737-1750 and references therein. A single polymer or a plurality of polymers may be deposited from solution to form layer 5. Where a plurality of polymers are deposited, they preferably comprise a blend of at least two of a hole transporting polymer, an electron transporting polymer and, where the device is a PLED, an emissive polymer as disclosed in WO 99/48160. Alternatively, layer 5 may be formed from a single second semiconducting polymer that comprises regions selected from two or more of hole transporting regions, electron transporting regions and emissive regions as disclosed in, for example, WO 00/55927 and US 6353083. Each of the functions of hole transport, electron transport and emission may be provided by separate polymers or separate regions of a single polymer. Alternatively, more than one function may be performed by a single region or polymer. In particular, a single polymer or region may be capable of both charge transport and emission. Each region may comprise a single repeat unit, e.g. a triarylamine repeat unit may be a hole transporting region. Alternatively, each region may be a chain of repeat units, such as a chain of polyfluorene units as an electron transporting region. The different regions within such a polymer may be provided along the polymer backbone, as per US 6353083, or as groups pendant from the polymer backbone as per WO 01/62869. Where insoluble layer 4 possesses hole or electron transporting property, a polymer or polymer region having this property may optionally be excluded from the polymer or polymers comprising layer 5.

The optical device prepared according to the method of the invention is preferably a PLED when the first and second electrodes inject charge carriers. In this case, layer 5 is a light emitting layer.

The optical device is preferably a photovoltaic device or photodetector when the first and second electrodes accept charge carriers. In this case, the second layer preferably comprises a polymer or polymers capable of hole and electron transport.

The inventors have surprisingly found that semiconducting polymers comprising fluorene repeat units without cross-linking (e.g. vinyl or ethynyl) moieties, become at least partially insoluble

when deposited to form insoluble layer 4. The present inventors have found that this insoluble layer forms (a) regardless of whether a PEDT/PSS layer is used or not and (b) in air or in a nitrogen only environment. The thickness of this insoluble layer may be increased by heat treatment of the layer following deposition of the polyfluorene. Without wishing to be bound by any theory, possible mechanisms for loss of solubility upon formation of the first layer include loss of solubilising groups attached to the 9-position of fluorene repeat units within the first semiconducting polymer or an adhesion to the surface that the first semiconducting polymer is deposited onto.

As outlined above, layer 4 is resistant to dissolution in the solvent used for deposition of layer 5 under the conditions typically employed for polymer deposition and solvent evaporation as used in the method of the present invention. Furthermore, layer 4 has been found to be resistant to dissolution when rinsed with said solvent. Although dissolution of layer 4 may be possible in said solvent under forcing conditions, it will be appreciated that layer 4 is sufficiently insoluble to enable formation of a plurality of electroactive organic layers in accordance with the method of the invention and the term "insoluble" should be construed accordingly.

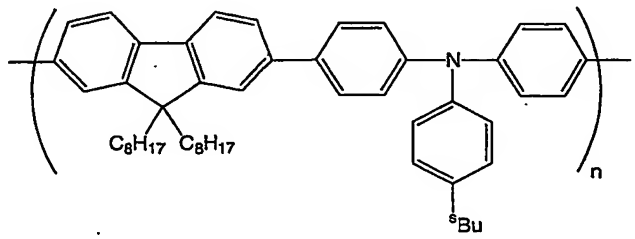
The described treatment has been found to improve efficiency and lifetime of PLEDs. Without wishing to be bound by any theory, the following factors may contribute to these observed increases:

- The first layer may act as a hole transporting, electron blocking layer when located between the anode and the second layer.
- Where a PEDT / PSS layer is used, the insoluble layer may be preventing ingress of protons from the acidic PSS material into the second layer. This may apply in particular where the polymer comprises basic units such as amines of formulae 1-6 or Het groups within the scope of formula 7, such as pyridyl, that are capable of accepting protons.
- The thinness of the layer, which is achieved in particular when the spin-rinsing step is employed, may enable charge blocking without any detriment to device performance that may result from a thicker layer, such as higher drive voltage.

Examples

General procedure

The invention is exemplified here using the polymer "F8-TFB", illustrated below and disclosed in WO 99/54385, as the first semiconducting polymer.



F8-TFB

The general procedure follows the steps outlined below:

1) Depositing PEDT / PSS, available from Bayer ® as Baytron P ® onto indium tin oxide supported on a glass substrate (available from Applied Films, Colorado, USA) by spin coating.

2) Depositing F8-TFB is by spin coating from xylene solution having a concentration of 2 % w / v.

3) Optionally heating the device at 180°C for 1 hour.

4) Optionally spin-rinsing the substrate in xylene to remove any remaining soluble F8-TFB

5) Depositing the second semiconducting polymer by spin-coating from xylene solution.

6) Depositing a NaF / Al cathode over the second semiconducting polymer in accordance with the process described in GB 0118258.3 and encapsulation of the device using a metal can as described in EP 0776147.

Parameters within this general process may be varied. In particular: the concentration of F8-TFB may be up to around 3 % w / v and a concentration of 0.5 % w / v may be used to provide a particularly thin film; the optional heating step may last for any length of time up to around 2 hours; and the optional heating step may be at any temperature up to around 220°C, but preferably above the glass transition temperature of the deposited polymer

<u>Example 1</u>

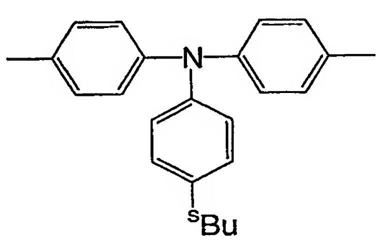
The general procedure above was followed using a blue electroluminescent polymer comprising 70 % 9,9-dioctylfluorene-2,7-diyl, 10 % 9,9-diphenylfluorene-2,7-diyl, 10 % "TFB" repeat unit and 10 % "PFB" repeat unit (TFB and PFB repeat units are illustrated below).

Figure 2 shows a plot of efficiency vs. bias for this device and comparison with a control device comprising the Blue Polymer wherein the insoluble layer of F8-TFB is not provided (i.e. omission of steps 2-4).

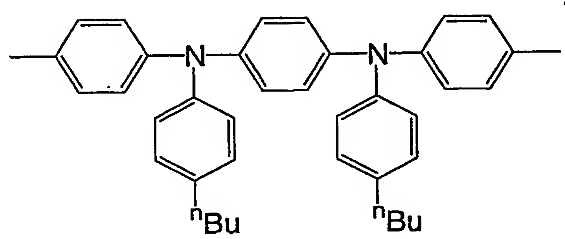
Example 2

The general procedure above was followed using a red electroluminescent polymer comprising 3% 4,7-bis(2-thiophene-5-yl)-2,1,3-benzothiadiazole repeat units (disclosed in WO 01/49768), 80% 9,9-dioctylfluorene-2,7-diyl, 30% 2,1,3-benzothiadiazole-4,7-diyl repeat units and 17% TFB repeat units, hereinafter referred to as "the Red Polymer".

Figure 3 shows a plot of efficiency vs. bias for this device and comparison with a control device comprising the Red Polymer wherein the insoluble layer of F8-TFB is not provided (i.e. omission of steps 2-4).



TFB



PFB

As can be seen from the referenced figures, inclusion of an insoluble layer according to the invention results in a substantial increase in device performance. Furthermore, lifetime (i.e. the time taken for the brightness of the device to decay to half its original brightness at a fixed current) and brightness of the device were at least not compromised, and in some instances improved, by inclusion of an insoluble layer.

The insoluble layer is formed with or without baking of the F8-TFB layer, however the thickness of the insoluble layer is greater when the F8-TFB layer is baked.

The second semiconducting polymer may be deposited without spin-rinsing of the first layer. This is preferably done where the first semiconducting polymer is deposited by spin-coating from dilute solution to form a first layer that is sufficiently thin for it to be rendered insoluble in its entirety, however the invention also encompasses deposition of the second semiconducting polymer wherein the first layer has been rendered only partially insoluble and the soluble portion

has not been removed. In this instance there will be some blending in the second layer of the first and second semiconducting polymers. Figure 4 shows efficiency vs. bias for two devices prepared according to the method of the invention using the Blue Polymer wherein one device is spin-rinsed and the other one is not. This figure shows that omission of the spin rinsing step has very little effect on device performance.

The examples above describe deposition of the first and second layers by spin-coating, however first and second layers according to the invention may be deposited by other techniques, in particular techniques suitable for making full colour displays such as inkjet printing as disclosed in EP 0880303, laser transfer as described in EP 0851714, flexographic printing, screen printing and doctor blade coating.

Application Example

Downconverter particles were attached to the outer surface of the substrate of the device of Example 1 (Blue Polymer) as described in Applied Physics Letters 80(19), 3470-3472, 2002 to provide a device capable of emitting white light.

Although the present invention has been described in terms of specific exemplary embodiments, it will be appreciated that various modifications, alterations and / or combinations of features disclosed herein will be apparent to those skilled in the art without departing from the spirit and scope of the invention as set forth in the following claims.

Claims

1. A method of forming an optical device comprising the steps of:

   - providing a substrate comprising a first electrode capable of injecting or accepting charge carriers of a first type;

   - forming a over the first electrode first layer that is at least partially insoluble in a solvent by depositing a first semiconducting polymer that is free of cross-linkable vinyl or ethynyl groups and is, at the time of deposition, soluble in a solvent;

   - forming a second layer in contact with the first layer and comprising a second semiconducting polymer by depositing a second semiconducting polymer from a solution in the solvent; and

   - forming over the second layer a second electrode capable of injecting or accepting charge carriers of a second type.

2. A method of forming an optical device comprising the steps of:

   - providing a substrate comprising a first electrode capable of injecting or accepting charge carriers of a first type;

   - forming a first layer over the first electrode by depositing a first semiconducting polymer comprising fluorene repeat units, the first semiconducting polymer being free of cross-linkable vinyl or ethynyl groups and being, at the time of deposition, soluble in the solvent;

   - forming a second layer in contact with the first layer and comprising a second semiconducting polymer by depositing a second semiconducting polymer from a solution in the solvent; and

   - forming over the second layer a second electrode capable of injecting or accepting charge carriers of a second type.

3. A method according to claim 1 comprising the step of heating the first layer prior to deposition of the second layer.

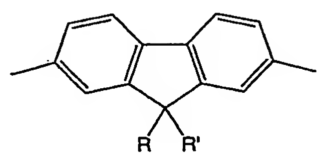
4. A method according to any one of claims 1-3 comprising a step prior to forming the second layer of washing the first layer with a solvent in which the first semiconducting polymer is soluble.

5. A method according to any preceding claim wherein the solvent is an aromatic hydrocarbon.

6. A method according to claim 5 wherein the solvent is an alkylated benzene.

7. A method according to claim 5 or 6 wherein the solvent is toluene or xylene.

8. A method according to any preceding claim wherein the fluorene repeat units comprise optionally substituted units of formula (I):



(I)

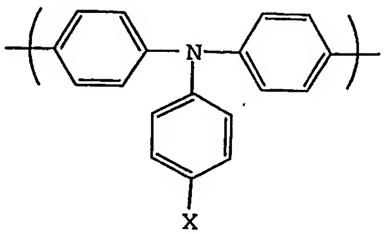
wherein R and R' are independently selected from hydrogen or optionally substituted alkyl, alkoxy, aryl, arylalkyl, heteroaryl and heteroarylalkyl, and at least one of R and R' is not hydrogen.

9. A method according to claim 8 wherein at least one of R and R' comprises an optionally substituted C_4-C_{20} alkyl group.

10. A method according to any preceding claim wherein the first electrode is capable of injecting holes and the second electrode is capable of injecting electrons.

11. A method according to claim 10 wherein the first semiconducting polymer comprises triarylamine repeat units.

12. A method according to claim 10 or 11 wherein the triarylamine repeat units are selected from optionally substituted repeat units of formulae 1-6:



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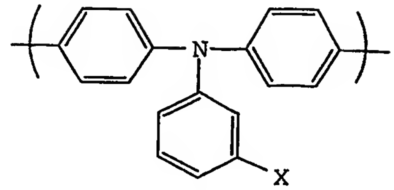

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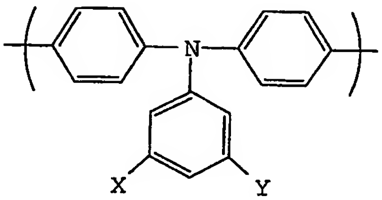

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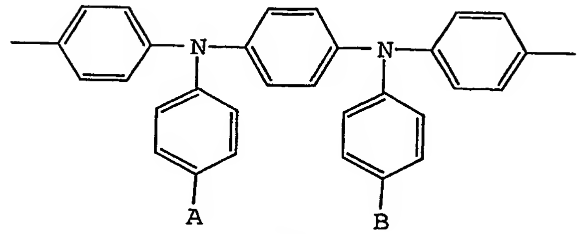

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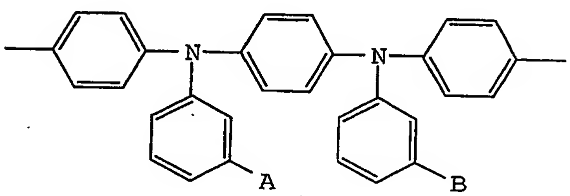

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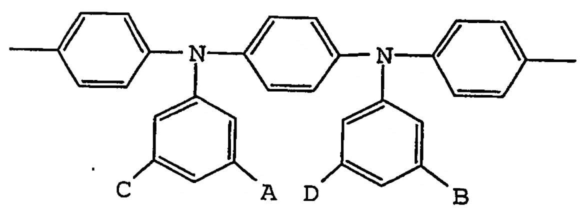

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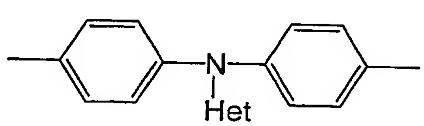
wherein X, Y, A, B, C and D are independently selected from H or a substituent group.

13. A method according to claim 12 wherein one or more of X, Y, A, B, C and D is independently selected from the group consisting of alkyl, aryl, perfluoroalkyl, thioalkyl, cyano, alkoxy, heteroaryl, alkylaryl and arylalkyl groups.

14. A method according to claim 11 wherein the triarylamine repeat unit is an optionally substituted repeat unit of formula 7:



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wherein Het is a heteroaryl.

15. A method according to claim 14 wherein Het is 4-pyridyl

16. A method according to any one of claims 11-15 wherein the first semiconducting polymer comprises a 1:1 regular, alternating copolymer of a fluorene repeat unit and a triarylamine repeat unit.

17. A method according to any one of claims 10-16 wherein a layer of conductive organic material is provided between the first electrode and the first layer.

18. A method according to claim 14 wherein the layer of conductive organic material is PEDT / PSS.

19. A method according to any preceding claim wherein the first layer has a thickness of less than 20 nm.

20. A method according to any preceding claim wherein the first layer has a thickness less than 10 nm, preferably in the range 3-10 nm.

21. A method according to any preceding claim wherein the second semiconducting polymer comprises a plurality of regions and comprising at least two of a hole transporting region, an electron transporting region and an emissive region.

22. A method according to claim 21 wherein the second semiconducting polymer comprises a hole transporting region, an electron transporting region and an emissive region.

23. A method substantially as described herein with reference to the drawings.

24. An optical device preparable according to the method of any preceding claim.

25. An organic electroluminescent display preparable according to the method of any one of claims 1-23

26. A blue light emitting electroluminescent display preparable according to the method of any one of claims 1-23.

27. A white light emitting organic electroluminescent display preparable according to the method of any one of claims 1-23.

28. An optical device comprising, in sequence:

- a substrate

- a first electrode capable of injecting or accepting charge carriers of a first type

- a first layer having a thickness less than 20 nm comprising a first semiconducting polymer that is insoluble in a solvent

- a second layer in contact with the first layer comprising a second semiconducting polymer that is soluble in the solvent

- a second electrode capable of injecting or accepting charge carriers of a second type.

29. A method of forming an optical device comprising the steps of:

    - providing a substrate carrying a conductive organic material capable of injecting or accepting holes and capable of donating protons;

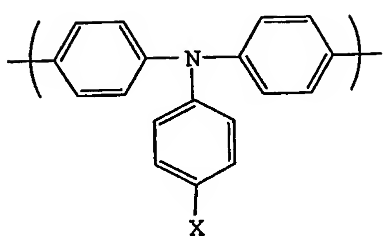
    - forming over the conductive organic material a first layer by depositing a first semiconducting polymer capable of accepting protons wherein the semiconducting polymer is, at the time of deposition, soluble in a solvent;

    - forming a second layer by depositing over, and in contact with, the first layer a second semiconducting polymer from a solution in the solvent; and

    - forming over the second layer a second electrode capable of injecting or accepting electrons.

30. A method according to claim 29 wherein the first semiconducting polymer comprises triarylamine repeat units.

31. A method according to claim 30 wherein the triarylamine repeat units are selected from repeat units 1-6:



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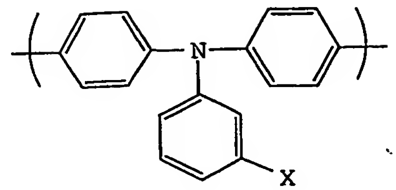

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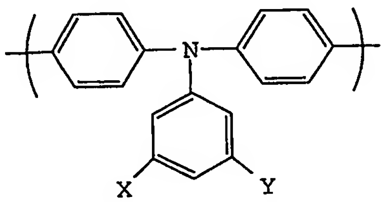

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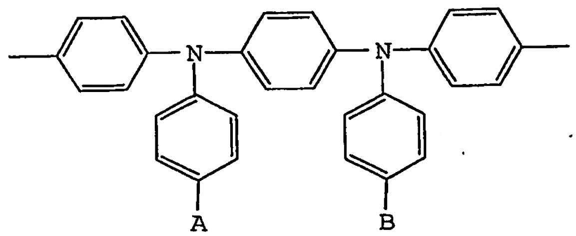

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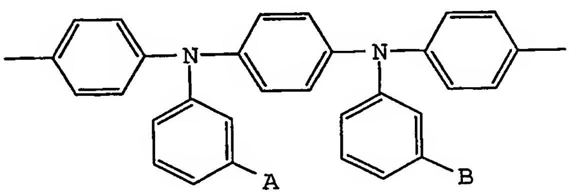

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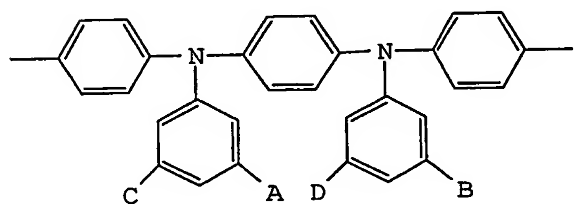

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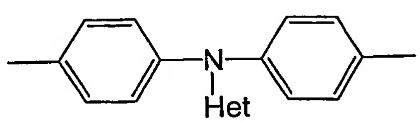
wherein X, Y, A, B, C and D are independently selected from H or a substituent group.

32. A method according to claim 31 wherein one or more of X, Y, A, B, C and D is independently selected from the group consisting of alkyl, aryl, perfluoroalkyl, thioalkyl, cyano, alkoxy, heteroaryl, alkylaryl and arylalkyl groups.

33. A method according to claim 30 wherein the triarylamine repeat unit is an optionally substituted repeat unit of formula 7:



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34. A method according to claim 33 wherein Het is 4-pyridyl.

35. A method according to any one of claims 30-34 wherein the first semiconductive polymer comprises a 1:1 regular, alternating copolymer of a fluorene repeat unit and a triarylamine repeat unit.

36. A method according to any one of claims 29-33 wherein a layer of inorganic material capable of injecting or accepting holes is provided between the substrate and the conductive organic material.

37. A method according to any one of claims 29-36 wherein the conductive organic material is PEDT / PSS.